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54 **Molecularly oriented thermoplastic member and process of forming same.**

57 A process of orienting a thermoplastic material, including the steps of forming the material into the desired shape, immediately cooling the material to below its glass transition temperature, reheating the material to a temperature above the glass transition temperature but below its melting temperature, drawing the material and cooling the material to ambient temperature while the material is under the drawing tension.

EP 0 321 176 A2

MOLECULARLY ORIENTED THERMOPLASTIC MEMBER AND PROCESS OF FORMING SAME

Background of the Invention5 Field of the Invention

The present invention relates to a process to orient a thermoplastic material and particularly a thermoplastic material which is absorbable in an animal body to increase its tensile strength and to products obtained by the process.

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Prior Art

Polymers which are absorbable in an animal body have been used to manufacture absorbable sutures for some time. Internal bone fixation devices made with absorbable polymers have also been described. For example, U.S. Patents Nos. 4,539,981 and 4,550,449 describe absorbable bone fixation devices made from a high molecular weight of polymer of L(-)lactide. The polylactide bone fixation devices disclosed in the aforementioned patents can be used to fabricate plates and screws as well as intramedullary rods and pins which are used to secure the ends of fractured bones in proximity of each other so that they may properly heal.

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Although the polylactide polymers are capable of being used for absorbable bone fixation devices it would be desirable if the absorbable polymer could be fabricated into plates, screws, pins and intramedullary rods which have even greater strength than the absorbable bone fixation devices described in the aforementioned patents.

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Various techniques have been known for increasing the strength of thermoplastic materials. For example, it has been known for years to heat and stretch thermoplastic sheets and tubes to impart molecular orientation and thereby increase strength. U.S. Patents Nos. 3,248,463; 3,541,189; 3,630,824; 3,775,523; 4,157,235; 4,209,484; 4,413,110; and 4,577,998 teach such techniques.

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SUMMARY OF THE INVENTION

The present invention provides a process for increasing the tensile strength thermoplastic materials such as polyesters and polyacrylics. The process is particularly useful in treating of polylactide and similar polymers that are absorbable in an animal body. The process of the present invention provides significantly increased tensile strength and flexural strength for the absorbable pins, rods and screws which can be formed from this polymer. Generally, the process includes the steps of melting an absorbable polymer by molding or extruding with little or no draw and immediately cooling the polymer to a temperature below its glass transition temperature to cause nucleation and to form a self-supporting member.

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The term "self-supporting" as used herein describes a member having sufficient structural rigidity that if the member is gripped or supported at one end thereof, the opposite end thereof will remain essentially in the same plane as the gripped or supported end. The term "self-supporting" is intended to distinguish over flexible, or limber, members (such as a suture, monofilament fiber, or the like) which, if gripped or supported at one end, will bend or droop such that the end of the member opposite the gripped or supported end will be substantially below the plane of the gripped or supported end.

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After the self-supporting member has been initially cooled, it is then heated to a temperature above its glass transition temperature and below its melting temperature while drawing it 2 to 12 times its original length. The member is then held under tension until it cools to room temperature. By processing the polymer in this manner, tensile strength increases of up to 800 percent can be achieved.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1 and 1A are side elevational and cross-sectional views of a preformed rod member;

Figs. 2 and 2A are side elevational and cross-sectional views of a rod formed in accordance with the process of the present invention;

Fig. 3 is a block diagram illustrating one form of the process of the present invention; and

Fig. 4 is a block diagram illustrating a second form of the process of the present invention.

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DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a process to significantly improve the tensile and flexural strengths of large profile, rigid polymers. The term "large profile" is intended to include circular rods having a diameter in excess of 1/32 inch as well as noncircular rods having dimensions of at least one side greater than 1/32 inch. These materials are also rigid as compared, for example, to a monofilament fiber of a similar diameter.

Referring now to Fig. 2, one form of a bone fixation device formed in accordance with the present invention is shown therein. Specifically, Fig. 2 illustrates a rod 10 having a first end portion 12, a second end portion 14, and a medial portion 16. Rod 10 is a solid, self-supporting member, and portions 12, 14 and 16 are circular in cross section (Fig. 2A). As will be evident from the ensuing description, the present invention contemplates that the formed, self-supporting member need not be solid, and may indeed be tubular. Furthermore, the formed, self-supporting member need not be circular in cross section, and may be oblong, triangular, hexagonal, or any other cross-sectional shape. Moreover, various different portions of any given self-supporting member may have different sizes and shapes.

In one specific form of the invention, the medial portion 16 of rod 10 has a length of 440 mm., and a diameter of 5.92 mm., while the end portions 12 and 14 have an average diameter of about 20 mm. End portions 12 and 14 are provided with a gripping means, such as grooves or ribs 18, to facilitate in holding the rod as it is drawn, from a preformed member, illustrated in Figs. 1 and 1A, to the configuration illustrated in Figs. 2 and 2A as described above.

With reference to Fig. 1, the preformed rod member 10A had an overall starting length of 98 mm., with a medial portion 16A having a length of 50 mm. and a diameter of 18 mm, and end portions 12A and 14A each having a length of 24 mm. End Portions 12A and 14A had a starting diameter of 20 mm. As will become evident from the following description, during the process of manufacturing rod 10, tension is applied to preformed rod 10A to draw it to its final configuration.

It should be understood that the dimensions set forth above are for purposes of example only, and are not meant to impose any limitation on the invention, except to the extent that such dimensions may be incorporated in the appended claims. Moreover, the illustration and description of rod 10 is not meant to impose any limitation on the shape or size of any bone fixation device, or devices, by subsequent processing steps; such as cutting, shaping, boring, drilling, threading, etc.

The present invention contemplates that bone fixation devices of the type described above may be formed either by a continuous process, e.g., extrusion, or by an intermittent process, e.g., injection molding. As will be appreciated, bone fixation devices formed by a process that include an extrusion step would have a substantially uniform initial cross-sectional shape; whereas, bone fixation devices formed by a process that includes a molding step could have a nonuniform shape, such as that illustrated in Figs. 1 and 2 wherein the end portions of the device are larger than the medial portion thereof.

The present invention specifically contemplates the bone fixation devices of the present invention are formed of a polymer that is absorbable in an animal body, such as the polylactide polymers disclosed in U.S. Patents Nos. 4,539,981 and 4,550,449, the disclosures of which are hereby incorporated herein in their entireties by this reference. The melting point of such polylactide polymers varies depending on their thermal history. For example, if the polymer of the aforementioned patents is ground into a powder and fed directly into an extruder, or into the cavity of an injection molding machine, it will melt at approximately 210°C. If the same polymer is melted and then formed into pellets, it will melt at a temperature of approximately 180°C. The highest temperature in the extruder, or in the cavity of the injection molding machine, may be just slightly higher, e.g., about 10°C higher, than the melting point of the polymer to avoid any degradation of the polymer.

Referring now to Fig. 3, a first embodiment of the process of the present invention, which includes a molding step, is illustrated schematically therein. In the initial step 20 of the process, the polymer is melted by raising it to a temperature above its melting point, e.g. raised to a temperature of 210°C, and injected into the cavity of an injection molding machine, where it is formed into the desired shape.

The formed member is removed from the cavity, and immediately cooled, as shown schematically at 22, at a controlled rate to a temperature below the glass transition temperature of the polymer. It has been found that it is important to not cool the formed members too quickly to prevent, or at least substantially

minimize, the formation of voids in the molded member. Likewise, it has been found that it is important to not cool the formed member too slowly to prevent, or at least substantially minimize, excessive crystallinity in the molded member. In accordance with a preferred embodiment of the present invention, immediately after the formed member is removed from the cavity of the injection molding machine, it is placed in an initial water bath at a temperature of about 65° C for a period of about 90 seconds, and thereafter placed in a secondary water bath at a temperature of about 42° C for a period of about 360 seconds. By quenching the formed member under these conditions, nucleation is promoted without excessive crystallinity and without the formation of voids. The cooled member will have the configuration shown in Fig. 1.

As an optional, but preferred, next step, the ends 12A and 14A of the formed and cooled member are annealed as shown schematically at 24 in Fig. 3. The annealing step may be performed, for example, by immersing the ends of the rod 10A in a glycerin bath at a temperature of about 100° C for a period of 10 minutes. It is important that the rod 10A not be retained in the annealing bath for too long of a period of time to prevent the medial portion 16A of the rod from crystallizing. It will be understood that the annealing step may be performed by inserting only the ends 12A and 14A in the annealing bath.

After the formed member has been cooled, and the ends optionally annealed, the formed member is reheated to a temperature above the glass transition temperature of the polymer, but below its melting temperature, as is shown schematically at 26 in Fig. 3. As will hereinafter be described, tension is applied to the formed member during at least a portion of the reheating step to molecularly orient the medial portion of the formed member. To this end, the ends 12A and 14A are gripped in the jaws of a conventional Instron testing machine, and a heated liquid is circulated throughout the interior of a chamber positioned between the jaws of the Instron machine to substantially uniformly heat the rod 10A to the desired temperature.

In accordance with one preferred embodiment of the invention, the heating liquid is water, although it should be understood that other inert liquids or gases are within the contemplation of the present invention, provided that adequate heat can be transferred to the rod 10A. The water is heated in a separate reservoir to a temperature of about 98° C and is introduced into the Instron tester at that temperature. The water exits the Instron tester at a temperature of about 90° C, and is effective to heat the rod 10A substantially uniformly to a temperature of about 87° C in about 3 minutes.

As the rod 10A is heated, it is subjected to solid state deformation. In this regard, the jaws of the Instron tester are moved relative to one another to apply tension to the medial portion of the rod, as is shown schematically at 28 in Fig. 3. It is important to control the speed of jaw movement in order to prevent breakage, and yet get the desired degree of molecular orientation before excessive recrystallization occurs. In accordance with one preferred embodiment of the invention the gripping jaws are initially moved apart at a rate of about 20 inches per minute until a load of about 250-260 pounds is applied to the rod. The pulling speed is then reduced to about 10 inches per minute, and is maintained at that rate until a load of about 300 pounds is applied to the rod. Thereafter the pulling speed is reduced to about 5 inches per minute and is maintained until a load of about 350 pounds is applied to the rod. Subsequently the pulling speed is gradually reduced to zero, when the desired length is obtained while continuing to maintain a load of about 350 pounds on the rod.

In accordance with one very important aspect of the present invention, once the rod has reached its final drawn length, the applied tension is retained. The heating liquid is then quickly drained from Instron tester, and cooling liquid is immediately circulated through the Instron tester as is shown schematically at 30 in Fig. 3. While other cooling fluids may be used, it has been found that circulating ice water at a temperature of about 6° C to about 15° C for a period of about 5 minutes has worked extremely well in quickly and uniformly cooling the drawn rod to the desired temperature. It is thought that the shrink energy of the rod during the cooling under tension step contributes significantly to the increase in ultimate tensile strength of the resulting product.

After the rod has been cooled, the tension is released and the rod is permitted to relax, as is shown schematically at 32 in Fig. 3. Thereafter the rod may be machined, as shown schematically at 34 in Fig. 3, as by cutting off ends 12 and 14, cutting medial portion 16 into shorter lengths, threading, etc.

EXAMPLES

Referring now to Fig. 4, a second embodiment of the process of the present invention, which includes an extruding step, is illustrated schematically therein.

In the process of Fig. 4, the absorbable polymer, such as the polylactide disclosed in U.S. Patents Nos. 4,539,981 and 4,550,449 can be ground or pelletized and fed to an extruder 36. The extruder would be

heated to a temperature slightly higher than the melting point of the polymer.

The polymer is immediately fed into a bath 38 of cold water at an initial temperature of 20° C which may subsequently rise to a temperature between about 45° and 50° C. This controls the formation of spherulites which are believed to be the nucleus from which crystals are formed during the orientation of the thermoplastic polymers. It is advantageous in the present process to rapidly cool the extruded polymer so that very small amounts of spherulites are formed and the polymer remains essentially amorphous.

The extruded polymer is then fed from tank 38 to a take-up device 40 which is operating at a speed equivalent to which the polymer is being extruded from the extruder. It is possible to practice the process of Fig. 4 with the pulling device operating at a speed such that the polymer is drawn from the extruder to the puller. This draw should be relatively low, i.e., no more than 3 to 1.

Puller 40 also operates as the restraining device for the extruded polymer during the remainder of the process. The extruded polymer is fed from take-up device 40 to a heating tank 42 that contains water or other fluid which is nonreactive with the polymer. The heating tank raises the temperature of the polymer to a temperature above the glass transition temperature of the polymer, but below the melting point of the polymer. The temperature is not critical within this range because the dimensions of the tank can be controlled to control the dwell time of the polymer in the tank.

The polymer is pulled through the heating tank by the puller 44 which is operating at a speed such that the central core of the polymer is heated to a temperature above the glass transition temperature of the polymer. In addition, the puller 44 draws the polymer so that the rod is reduced in its cross-sectional dimension as it is extended in length. The draw ratio at this stage of the process is between 2 and 10. The temperature in the tank 42 and the pull rate must be controlled to avoid excessive crystallization of the polymer as it is drawn. The extruded polymer is then maintained under tension until it reaches room temperature. If the tension is relaxed prior to the extruded polymer reaching room temperature, the polymer has a tendency to bend and buckle and lose its straight shape. The puller 44 may be cooled, if desired, with cold water. This will reduce the amount of time necessary to keep the product under tension.

EXAMPLE 1

This example illustrates the preparation of an unoriented control sample. Pelletized, high molecular weight polylactide is extruded through a commercial extruder. No tension is applied to the polylactide rod as it exits the extruder nozzle. The polylactide rod is quenched in a water spray and then is passed through an 8 foot long water bath maintained at a temperature of 60° C in a relaxed state. This corresponds to a draw ratio of 1. The sample was then tested and had the following properties:

Ultimate tensile strength, mpa	-	22.8
Secant modulus, mpa	-	1564
Elongation percent	-	4

EXAMPLE 2

This example illustrates the effect of applying tension to the polylactide rod after it is extruded, but before it is quenched.

High molecular weight polylactide pellets as used in Example 1 were extruded under the same conditions as set forth in Example 1. Tension was applied to the polylactide rod as it came out of the nozzle of the extruder. The draw ratio was 4.4:1. The material was cooled to room temperature without passing through the 60° C bath as in Example 1. The product was tested for tensile strengths and had the following properties:

Ultimate tensile strength, mpa	-	25.5
Secant modulus, mpa	-	1205
Elongation percent	-	22

This sample did not have a significantly different tensile strength than the sample of Example 1.

EXAMPLE 3

This example illustrates the effect of a hot water heating treatment after deformation without a nucleation or quenching step.

- 5 The polylactide pellets used in Example 1 were extruded at a draw ratio of 4.4:1 as in Example 2. The extruded polylactide was heat-treated by passing it through a heating tank containing a water bath at 60 °C in a relaxed state. Tensile tests were performed with a sample with the following results:

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Ultimate tensile strength, mpa	-	68.6
Secant modulus, mpa	-	1539
Elongation percent	-	11

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EXAMPLE 4

- This example illustrates the process of the present invention. Polylactide pellets of the same type used in Example 1 were extruded through a 0.75 inch diameter die. The extruded rod was immediately quenched by spraying cold water of a temperature of approximately 20 °C while the rod was pulled to a diameter of 0.48 inches. This corresponds to a draw ratio of 2.4:1. The polylactide rod was reheated to a temperature immediately above its glass transition temperature. During the heating process the rod was subjected to a further draw with a draw ratio of 4.0:1. The sample was cooled while it was kept under tension. Once the rod was cooled to room temperature, the tension was relaxed. The tensile test results of this sample were as follows:
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Ultimate tensile strength, mpa	-	187
Secant modulus, mpa	-	7409
Elongation percent	-	82

- By comparing Example 1 to Example 2 it is evident that while the application of strain prior to nucleation or quenching does not significantly improve the tensile strength, it does significantly increase the elongation value. By comparing Example 3 to Example 2 it is evident that while the solid state deformation without nucleation does not help the strength significantly, the subsequent heat treatment improves both the strength and the modulus. When Example 4 is compared to Examples 1-3, the superior strength of products formed in accordance with the present invention is readily apparent.
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EXAMPLE 5

This example illustrates the present invention when the preformed member is obtained by injection molding.

- Further injection molded polylactide samples were prepared in accordance with the process described before in connection with Figs. 1, 2 and 3, and evaluated to determine the effect that various draw ratios had on ultimate tensile strength. The results of this evaluation are set forth in the following table:
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Sample	Draw ratio	Ultimate tensile strength (mpa)
Control	1	62
1	2.63	90
2	3.13	141
3	3.75	223
4	4.65	245
5	5.35	294
6	6.34	317
7	6.48	279
8	6.8	295
9	6.82	296
10	7.22	309
11	7.82	326
12	7.96	335
13	8.4	351
14	8.82	338
15	10.61	492

From the above, it is clear that in accordance with the present invention as the draw ratio increases there is a direct and substantially proportionate increase in ultimate tensile strength.

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While the invention has been described in conjunction with specific embodiments thereof, it is evident that many alternatives, modification and variations will be apparent to those skilled in the art in light of the above description. Accordingly, it is intended to embrace all such alternatives, modification and variations that fall within the spirit and broad scope of the appended claims.

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EXAMPLE 6

This example illustrates the use of the present invention to make oriented, high strength rods from nonabsorbable thermoplastic polymer.

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The polymer used in this example was a clear impart acrylic resin RSA-3G obtained from Richardson Polymer Corporation of Connecticut. This polymer was injection molded at 240° C into preformed members shown in Figure 1. Then it was oriented using the same process as outlined in Example 5 except the samples were made at a draw ratio of 3.4. The test results of the nonoriented and the oriented samples of this polymer are shown below:

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Sample	Draw ratio	Ultimate tensile strength, MPa
Control	1	58
1	3.4	122

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The results indicate that the strength of this polymer has been doubled by processing it according to the present invention.

50 Claims

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1. The process of forming a self-supporting high strength thermoplastic member comprising the steps of: providing a thermoplastic polymer capable of being absorbed in an animal body; melting the thermoplastic polymer; cooling the thermoplastic polymer to a temperature below its glass transition temperature to cause nucleation and to form a self-supporting member; reheating the self-supporting member to a temperature above the glass transition temperature of the thermoplastic polymer, but below its melting temperature; applying tension to the self-supporting member during said reheating step; cooling the

reheated self-supporting member while maintaining the tension applied thereto; and discontinuing the application of tension after the self-supporting member has cooled to permit the self-supporting member to relax.

2. The process of Claim 1 wherein said thermoplastic polymer is melted by processing it in an extruder.

5 3. The process of claim 1 or claim 2 wherein tension is applied to said member during said initial cooling step.

4. The process of any one of claims 1 to 3 wherein the initial cooling step is performed by exposing the member to a cooling fluid.

5. The process of Claim 4 wherein said cooling fluid is air.

10 6. The process of Claim 4 wherein said cooling fluid is water.

7. The process of Claim 6 wherein the water is applied by spraying.

8. The process of Claim 6 wherein the member is cooled by immersing it in a water bath.

9. The process of Claim 1 wherein said thermoplastic polymer is melted by processing it in an injection molder.

15 10. The process of Claim 9 wherein the thermoplastic polymer is molded into the shape of a rod.

11. The process of claim 10 wherein the ends of said rod are annealed before said reheating step.

12. The process of any one of claims 1 to 11 wherein said member is preheated during said reheating step prior to the application of tension.

13. The process of any one of claims 1 to 12 wherein the step of applying tension is performed by effecting relative longitudinal movement between two spaced points on said member at a given rate until a predetermined load is applied, and then gradually reducing the rate of said relative movement.

14. The process of any one of claims 1 to 13 wherein the final cooling step is performed by exposing the member to a cooling fluid.

15. The process of Claim 14 wherein the cooling fluid is water.

25 16. The process of Claim 3 wherein the tension applied to said member during said initial cooling step is at a draw ratio of 3 or less.

17. The process of Claim 16 wherein the tension applied to said member during said reheating and final cooling steps is greater than the tension applied during said initial cooling step.

30 18. The process of claim 16 wherein the tension applied to said member during said reheating and final cooling step is at a draw ratio of between 3 and 10.

19. The process of forming a self-supporting high strength thermoplastic member comprising the steps of: melting a high molecular weight polylactide polymer; forming the molten polylactide polymer into a desired shape; immediately cooling the formed member at a controlled rate to a temperature below the glass transition temperature to cause nucleation and to form a self-supporting member; reheating the self-supporting member to a temperature above the glass transition temperature of the polylactide polymer but substantially below its melting temperature; applying tension to the self-supporting member at a controlled rate during at least a portion of said reheating step at a draw ratio of between about 2 to about 12 times the original formed length of the member to thereby obtain a high degree of molecular orientation in the self-supporting member; cooling the reheated self-supporting member to ambient temperature while maintaining the same level of tension that was applied during the reheating step; and discontinuing the application of tension after the self-supporting member has cooled to permit said self-supporting member to relax.

20. A self-supporting high strength member formed of a thermoplastic polymeric material capable of being absorbed in an animal body, said self-supporting member having a shape defined by final length and cross-sectional dimensions, the final dimensions of said self-supporting member being substantially different than the initial dimensions of a preformed member, the final length of said self-supporting member being at least twice the initial length of said preformed member and the final cross-sectional dimension of said self-supporting member being less than 50% of the initial cross-sectional dimension of said preformed member, said self-supporting member being highly molecularly oriented and having an ultimate tensile strength substantially greater than the ultimate tensile strength of said preformed member.

50 21. A self-supporting member as defined in Claim 20 wherein said member is formed of a polylactide polymer.

22. A self-supporting member as defined in Claim 20 wherein said member is formed of extruded polylactide.

55 23. A self-supporting member as defined in Claim 20 wherein said member is formed of molded polylactide.

24. A large profile, self-supporting, high-strength bone fixation device formed of a high molecular weight polymer of L(-)lactide capable of being absorbed in an animal body, said bone fixation device having a shape defined by a final length and cross-sectional dimensions, the final dimensions of said bone fixation

device being substantially different than the initial dimensions of a preformed member, the final length of said bone fixation device being at least twice the initial length of said preformed member and the final cross-sectional dimension of said bone fixation device being less than 50% of the initial cross-sectional dimension of said preformed member, said bone fixation device being highly molecularly oriented and
5 having an ultimate tensile strength substantially greater than the ultimate tensile strength of said preformed member.

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FIG-1A

FIG-2A

FIG-1

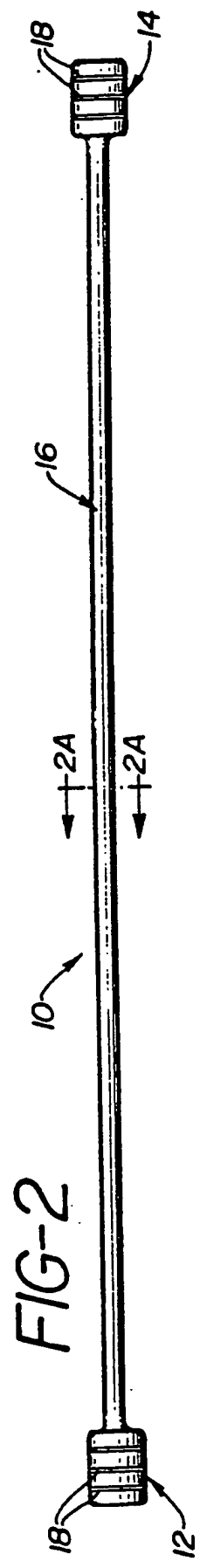
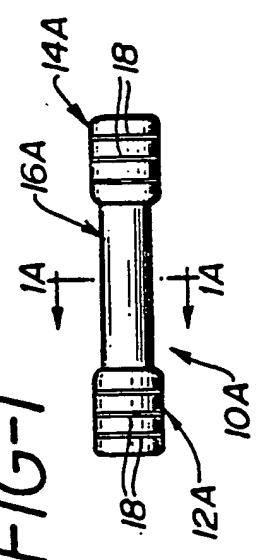
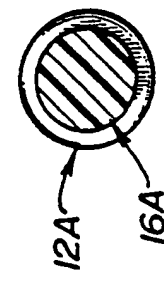
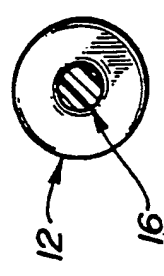


FIG-3

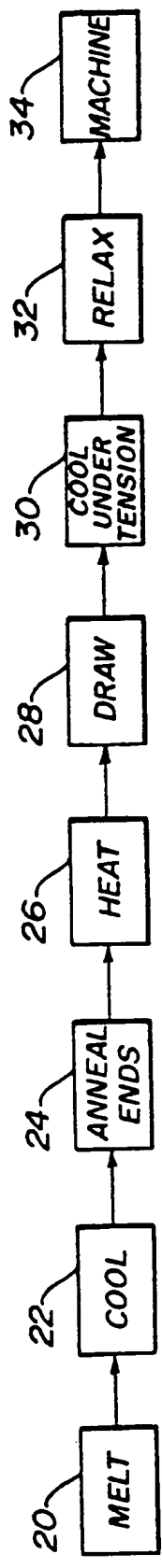
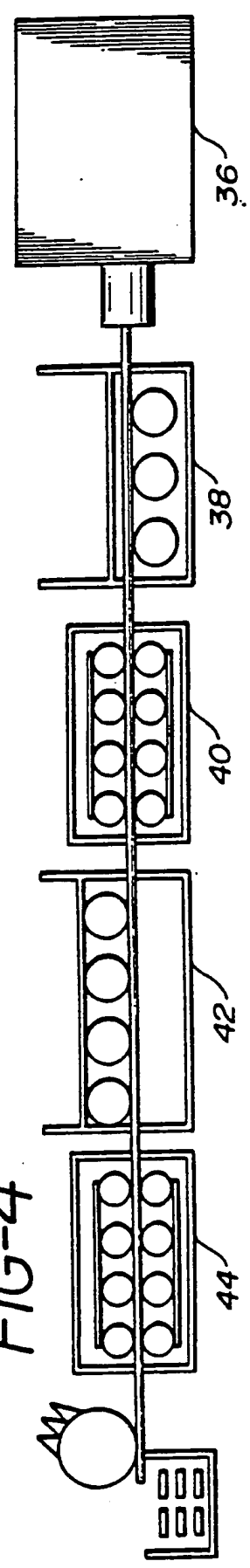


FIG-4



EP0321176

Publication Title:

Molecularly oriented thermoplastic member and process of forming same.

Abstract:

A process of orienting a thermoplastic material, including the steps of forming the material into the desired shape, immediately cooling the material to below its glass transition temperature, reheating the material to a temperature above the glass transition temperature but below its melting temperature, drawing the material and cooling the material to ambient temperature w

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hile the material is under the drawing tension.

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